

# An Examination of Methods for the Measurements of Reactive Gaseous Mercury in the Atmosphere

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Reactive gaseous Hg (RGHg), usually assumed to be  $\text{HgCl}_2$ , may dominate the total Hg depositional flux due to its higher surface reactivity and water solubility. Three methods are currently used for RGHg sampling: multi-stage filter packs, refluxing mist chambers, and KCl-coated denuders, but none of these methods are considered standard. Field comparisons were performed at Chesapeake Biological Laboratory (CBL) to test if these methods could give comparable results. Mist chambers and denuders were operated continuously for 24 h in some cases to observe the diurnal variation. All methods demonstrated the dynamic fluctuation of atmospheric RGHg, ranging from a few picograms per cubic meter to more than 500 pg/ $\text{m}^3$ . These methods also reported similar temporal RGHg trends. At low RGHg levels, the denuder tended to report higher values of RGHg relative to the filter pack, while mist chamber values were generally in agreement with the filter pack. Discrepancy among methods was more significant under higher RGHg levels. Considering the uncertainties associated with these methods, our data suggest that these methods did produce comparable results. The 24-h continuous measurements showed that RGHg was usually undetectable at night. However, our data also suggest factors in addition to photochemistry, such as movement and mixing of air masses, are influencing the distribution of RGHg at CBL.

## Introduction

Although typically present at low concentrations in the environment (e.g., ng/ $\text{m}^3$  level in the air and ng/L level in rainwater), Hg is ubiquitous because of its anomalous physical and chemical properties. Mercury is the only metal existing in liquid phase at normal room temperature. Elemental Hg has a relatively high vapor pressure of 0.246 Pa at 25 °C (1) and a low Henry's law constant of 0.11 M/atm at 20 °C (2). Therefore, while other metal pollutants tend to exist in the particulate phase in ambient air, Hg mainly exists in the gaseous phase.

Methylation of inorganic Hg in aquatic environments and subsequent bioaccumulation in fish through the food chain is a major human health and environmental concern due to the toxicity of methylmercury. The atmosphere is an important source of Hg to surface waters and terrestrial environments, especially in remote areas where there are no local sources (3–8). For example, according to a recent

estimate, the open ocean currently receives 90% of its Hg input through wet and dry atmospheric deposition (9). Both natural and anthropogenic sources contribute to the Hg in the atmosphere. According to the U.S. EPA estimate, the annual global input of Hg to the atmosphere from all sources is 5500 ton (10). Nriagu and Pacyna (11) estimated that the global anthropogenic Hg emission in 1983 was in the range of 1000–6000 ton. In the United States, 158 ton of anthropogenic Hg was emitted in 1994–1995 (10), and about 87% of these Hg emissions were from combustion sources. Combustion sources, including coal combustion and waste incineration, are also the major sources of anthropogenic emissions globally (12).

Speciation of emitted Hg is important in determining its transport and fate in the atmosphere. The physical or chemical speciation of naturally emitted Hg has not received much attention, although it is assumed to be elemental Hg primarily. On the other hand, the speciation of Hg in anthropogenic emissions has been categorized in more recent inventory estimates. Divalent Hg is the major form in waste incineration emissions, while both elemental and divalent forms are significant constituents in coal combustion emissions (13). On the basis of the chemical and physical properties, three species can be distinguished in the anthropogenic Hg emissions and in the atmosphere: gaseous elemental Hg ( $\text{Hg}^0$ ), gaseous divalent Hg (or reactive gaseous Hg, RGHg), and particulate Hg ( $\text{Hg-P}$ ). Particulate Hg is thought to deposit quickly after being emitted from stacks, and its residence time in the air depends on particle size and usually ranges from a few hours to a few weeks. Therefore,  $\text{Hg-P}$  is not considered to participate in global Hg transport, although it may be important in the local or regional Hg budget. The speciation of RGHg is current unknown, but it is usually assumed to be  $\text{HgCl}_2(\text{g})$  or other mercuric halides, which have a higher surface reactivity and water solubility than  $\text{Hg}^0(\text{g})$ . Because of the higher surface reactivity and water solubility, RGHg can be scavenged by both dry and wet deposition more efficiently than  $\text{Hg}^0$  and  $\text{Hg-P}$ . It is therefore removed rapidly from the atmosphere with an atmospheric residence time that is less than that of  $\text{Hg}^0$  and  $\text{Hg-P}$ . Hence RGHg is also not considered to be important in long-range transport of Hg. On the other hand,  $\text{Hg}^0$  is relatively stable in the atmosphere with a residence time between 6 month and 2 yr (14, 15). This residence time is sufficient for  $\text{Hg}^0$  to be transported and well-mixed at least within each hemisphere. Consequently, in the atmosphere, Hg generally exists in gaseous elemental form with only a few percent of the total typically present as  $\text{Hg-P}$  and/or RGHg (16, 17). Nevertheless, air could be enriched with RGHg and  $\text{Hg-P}$  in the vicinity of point sources.

Once in the atmosphere, Hg undergoes various physical and chemical transformations before being removed. Only a few chemical reactions of Hg have been studied in the laboratory under conditions relevant to the atmosphere. Lin and Pehkonen (18) have published a detailed review discussing these reactions; thus, only a brief summary is given here. Elemental Hg can react with several oxidants in the aqueous phase (e.g., cloudwater), including  $\text{O}_3$  (19, 20), OH radical (21), and  $\text{HOCl/OCl}^-$  (22), to form divalent Hg. Hydrogen peroxide is not an important oxidant for Hg, but it can be a source of the radicals that react with Hg (23). On the other hand,  $\text{SO}_3^{2-}$  (24) and  $\text{HO}_2$  radicals (25) can reduce divalent Hg in the aqueous phase. Photoreduction of  $\text{Hg}(\text{OH})_2$  in the aqueous phase is another reduction pathway (26). In the gaseous phase,  $\text{O}_3$ ,  $\text{H}_2\text{O}_2$ , and  $\text{NO}_3$  and other gaseous radicals are all able to oxidize  $\text{Hg}^0$  (27–29) although

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it is not clear if there is any significant gaseous phase reduction of divalent Hg occurring in the atmosphere.

Even though  $\text{Hg}^0$  is the dominant form in ambient air, RGHg may dominate the total Hg depositional flux because of its higher surface reactivity and water solubility. Several modeling studies and sensitivity analyses regarding the transport and removal of atmospheric Hg have validated the necessity of better understanding the Hg speciation in emissions and in the atmosphere (30–33). Reliable sampling and measurement of RGHg is thus critical for a good estimate of the Hg depositional flux. Techniques for total gaseous Hg (TGHg, mainly  $\text{Hg}^0$ ) sampling and measurement are now quite mature; however, RGHg sampling methods are still under development. Currently there are at least three collection methods used for RGHg sampling: a multi-stage filter pack method (34), a refluxing mist chamber method (35–37), and a KCl-coated denuder method (38, 39). None of these methods are considered standard, and each method has advantages and disadvantages. For the filter pack method, Hg-P is removed from the air stream by the first two Teflon filters with the RGHg collected by the cation-exchange membranes positioned behind. Therefore, both Hg-P and RGHg are collected simultaneously. The main disadvantage of this method is the long sampling time required, usually 24 h, to obtain sufficient RGHg for analysis since the flow rate is relatively low. Volatilization of collected Hg-P and its subsequent collection by the cation-exchange membrane is another concern, although it has been demonstrated not to be a problem for other volatile species, such as  $\text{HNO}_3$ , HCl, and  $\text{NH}_3$  (40). If oxidation of  $\text{Hg}^0$  by heterogeneous reactions occurred on the filter surface, this would also cause a positive artifact. The extent of this problem is not clear. Adsorption of RGHg onto the particle-removing filters at low flow rates is also possible. For example, adsorption of  $\text{HgCl}_2$  onto quartz fiber filters has been observed in the lab (34), but Stratton et al. (37) found no bias in field measurements with or without filters in front of the mist chamber. While there is little field evidence to support adsorption, if these types of artifact did happen in field they would jeopardize almost all the historical Hg-P and filter pack RGHg measurements.

The refluxing mist chamber allows higher flow rates and thus shorter sampling time, usually between 30 and 120 min. However, the scrubbing solution (dilute HCl) not only removes RGHg from the air stream but also other water-soluble gases, some of which may react with  $\text{Hg}^0$  or RGHg and cause either positive or negative artifacts. The composition of the scrubbing solution, especially the concentration of chloride, does influence the amount of RGHg collected (37). A single-stage Teflon filter pack can be attached to the chamber inlet to remove particles. Again, this particle-removing filter may cause artifacts that have been discussed before.

The denuder method also allows higher flow rates and shorter sampling time. Two types of denuders have been developed: the tubular denuders (38) and the annular denuders (39). For the annular denuders, particles larger than  $2.5\ \mu\text{m}$  are removed from the air stream by a cyclone before entering the denuder, and smaller particles pass through without deposition under the proper flow rate because of the laminar conditions inside the denuder. Adsorption of  $\text{Hg}^0$  is a potential positive artifact for the denuder method. Xiao et al. (38) determined the  $\text{Hg}^0$  breakthrough efficiency by spiking gaseous  $\text{Hg}^0$  into the tubular denuder inlet and found that only 98.7% of the spike was recovered downstream. This non-100% breakthrough efficiency was interpreted as a result of system error and another experiment was conducted, which demonstrated that the denuder did not adsorb  $\text{Hg}^0$  to any degree in the laboratory. The quality of KCl coating is important to collection efficiency and it may change over time when operated in the field, with resultant

changes in  $\text{Hg}^0$  adsorption. Just 1%  $\text{Hg}^0$  adsorption would be enough to compromise the measured RGHg concentration.

Although all the sampling methods appeared promising, it is difficult to directly compare RGHg data generated by various groups using different methods, considering the uncertainties associated with these methods in the field. Therefore, the main purpose of this study was to demonstrate if these sampling methods gave comparable results under the same environmental conditions. Instead of testing these systems in the laboratory, all experiments were operated under field conditions with systems running side by side. This paper describes the results of 16 field sampling sessions at the Chesapeake Biological Laboratory (CBL) in 1998 and 1999. Seven of the 16 sampling sessions were operated continuously for 24 h to see if any diurnal patterns could be observed.

## Methods and Sites

All samples were collected on the research pier of CBL (Figure 1), which is located at the mouth of Patuxent River on the western shore of the Chesapeake Bay, about 80 km SSE of Washington, D.C. A 2339 MW power plant is located in the north of CBL, about 30 km away, which burns coal, oil, and gas. Another power plant (1412 MW), which also burns coal and oil, is about 50 km west of CBL.

Three methods were employed for atmospheric RGHg collection: a 5-stage filter pack, a refluxing mist chamber, and a KCl-coated annular denuder. The filter pack method has been described previously (34, 41). Acid-cleaned open-face 5-stage Teflon filter holders were used in this study. Two  $47\ \text{mm} \times 0.45\ \mu\text{m}$  Teflon filters and three  $47\ \text{mm}$  cation-exchange membranes were housed in the Teflon filter holder. The first Teflon filter removed the particles while the second filter acted as a backup (or blank). Similarly, the first ion-exchange membrane collected the RGHg sample with the second membrane acting as a backup. The third membrane was to prevent backward diffusion of RGHg from the pump. Incoming air first flowed through the Teflon filters to remove particles prior to the ion-exchange membranes that were positioned behind the Teflon filters. A longer sampling time was necessary for the filter pack method because the airflow rate (3–5 L/min) was low and only  $6\ \text{m}^3$  of air flowed through the system in a 24-h period. Sampling time varied between 6 and 24 h during this study. This allowed  $1.5\text{--}6\ \text{m}^3$  of air to be sampled.

A detailed description of the refluxing mist chamber has been published (35–37). Briefly, airflow through the quartz chamber creates a fine mist that subsequently scavenges soluble species from the air stream. In this study, contrary to the studies of Lindberg and Stratton (35–37), a  $0.45\ \mu\text{m}$  Teflon filter was placed in front of the air inlet to remove particles. Stratton et al. (37) have recently shown that use of a prefilter does not compromise the RGHg collection by the mist chamber. Another Teflon filter was placed on top of the quartz chamber to reduce water loss.

The mist chamber was filled with 25 mL of 0.05 M HCl as the scrubbing solution. A flow rate of 10 L/min was used, and the sampling time varied between 75 and 120 min, resulting in the sampling of  $0.75\text{--}1.2\ \text{m}^3$  of air. The remaining solution was transferred to an acid-cleaned Teflon vial at the end of each sampling period. Another 25 mL of 0.05 M HCl was then added to the chamber and aspirated for another 30 s to rinse the chamber surface to wash off any adsorbed Hg. The rinse was transferred to a separate vial. The sample solution and the rinse were analyzed together in 1998 but were analyzed separately in 1999. The results from 1999 showed that on average 11% of the collected Hg was left in the chamber each time it was emptied, a value that agrees well with published data (10%, ref 35).

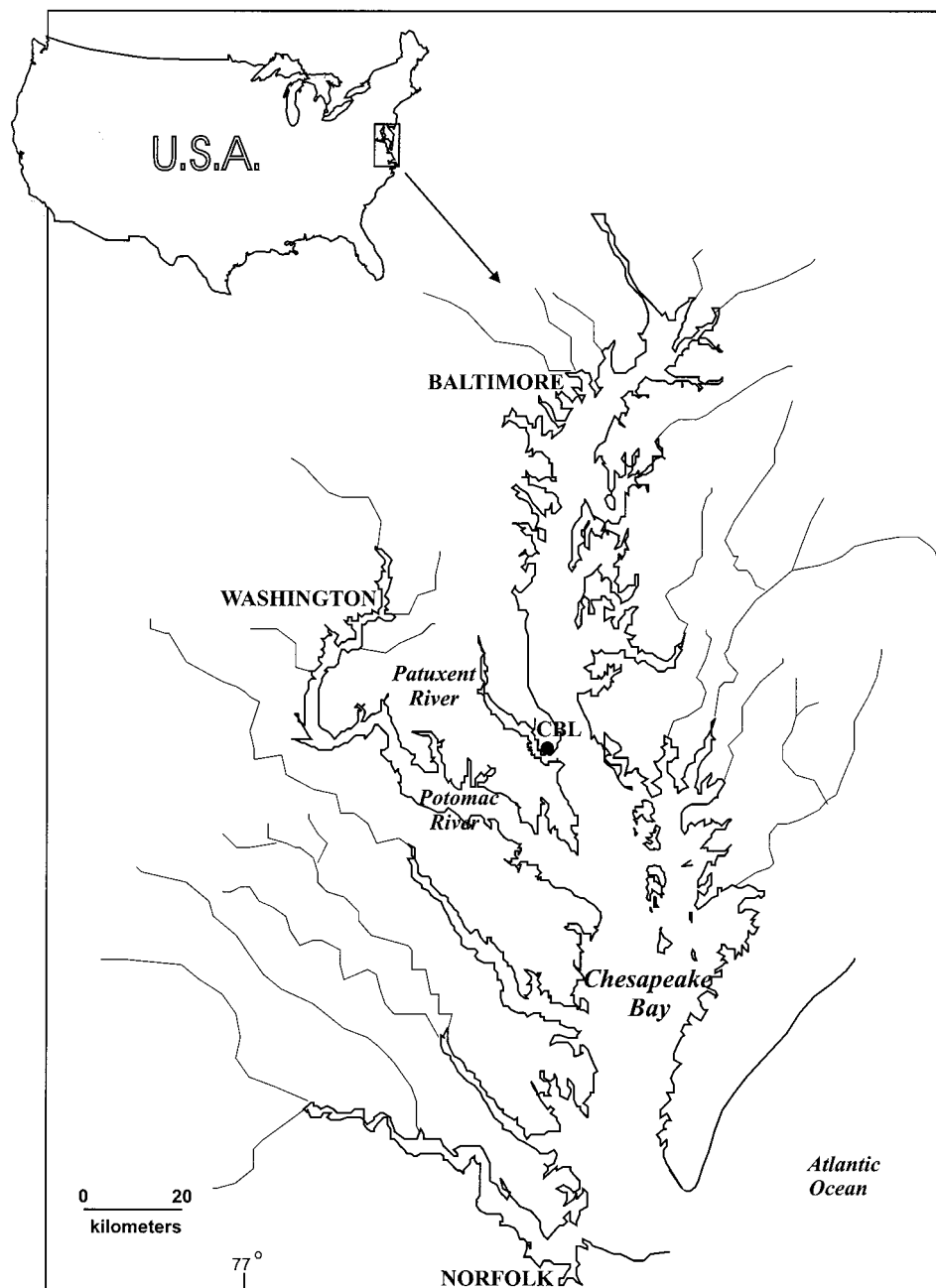


FIGURE 1. Map of Chesapeake Biological Laboratory.

Since the mist chambers were exposed to sunlight in the field, the possibility of photochemical conversion of  $\text{Hg}(\text{Hg}(0) \leftrightarrow \text{Hg}(\text{II}))$  inside the chamber was a concern. While no significant photochemical effects were observed at inland sites in the presence of ozone (35, 37), we tested the potential for photochemical effects with two mist chambers running side by side at CBL in the August of 1999: a regular chamber exposed to sunlight and one covered with aluminum foil. Amounts of RGHg collected by these two chambers were generally within a factor of 2 to each other, and there was no pattern indicating collection bias in either chamber. Therefore, our preliminary results suggest that sunlight does not substantially influence the performance of the mist chambers at CBL. As suggested by Stratton et al. (37), in-chamber reactions with other reactive species besides ozone, such as reactive halogen species, could produce a positive artifact in the mist chambers. We have not investigated these potential reactions, and researchers opting for this method of collection of RGHg should more thoroughly investigate

the potential for artifact formation, especially in locations such as the marine boundary layer where reactive halogens are more readily formed.

Information regarding preparation of KCl-coated annular denuders was offered by Robert Stevens and Matt Landis (personal communication) and is briefly summarized here. The denuders used in this study were manufactured by URG Corporation. For this study, denuders were first cleaned by soaking in concentrated  $\text{HNO}_3$  for 1 week and then in dilute HCl for 1 week. The acid-cleaned denuders were then rinsed with Milli-Q water and air-dried in a clean room. These pretreated denuders were soaked in saturated KCl solution for 30 min at room temperature. Excess water inside the denuders was removed by heating at a temperature around  $500^\circ\text{C}$  with argon gas flowing through the denuder. Tiny crystals of KCl covered the inner denuder surfaces after being heated. When in operation, particles greater than  $2.5\ \mu\text{m}$  were removed by a cyclone attached to the air inlet. Smaller particles flowed through the denuder because of the laminar



flow conditions maintained under the proper flow rate conditions. Flow rate was maintained at 10 L/min with sampling times between 100 and 120 min, resulting in 1–1.2 m<sup>3</sup> of air sampled. Denuders were heated at 500 °C for 30 min to remove any Hg residue before deployment. After field sampling, the denuder was connected to a blanked gold trap and heated at 500 °C for 45 min to release all the adsorbed Hg as Hg<sup>0</sup>. The Hg released was captured by the gold trap. The same denuder was then connected to another blanked gold trap and heated for another 15 min to determine a lab blank. This procedure was followed for every sample. Argon gas was used as the carrier gas, and the flow rate was maintained at 30 mL/min for the denuder blanking and the thermal release of Hg procedures.

A total of 16 ambient RGHg sampling studies were done on the CBL research pier between July 1998 and October 1999. These included 11 filter pack and mist chamber comparisons, 2 filter pack and denuder comparisons, and 3 overall comparisons. Total gaseous Hg (TGHg), sampled during 9 of the 16 events simultaneously, was collected by pumping air through gold-coated quartz sand traps (42). Air inlets of all sampling apparatus were 1.5–2 m above the water surface.

Mercury was quantified by cold vapor fluorescence spectrometry (CVAFS) using the standard technique for Hg analysis at low level (43). Total gaseous Hg samples were analyzed directly. Filter samples were first oxidized by 0.2 N BrCl solution for at least 30 min and then pre-reduced using hydroxylamine hydrochloride prior to quantification by SnCl<sub>2</sub> reduction CVAFS (6). Mist chamber samples were analyzed by SnCl<sub>2</sub> reduction CVAFS without addition of BrCl and hydroxylamine hydrochloride. Denuder-adsorbed RGHg samples were thermally reduced to Hg<sup>0</sup> and captured by a gold trap, which was later quantified by CVAFS. The analytical detection limits for the filter pack, mist chamber, and denuder methods are 7, 5, and 15 pg/m<sup>3</sup>, respectively. For the denuders, many of the blanks (54%; *n* = 54) were less than 1 pg (undetectable), and the reported higher detection limit is the result of high variability associated with occasional high value on blanking the denuder. These high blanks likely resulted from the incomplete desorption of the sample Hg during the analysis phase of the previous sample or from incomplete blanking of the gold trap prior to use, as both the denuders and gold traps were used repeatedly. Thus, the reported value is conservative. Precision tests have been performed for the filter pack method with three filter packs running side by side in the field at CBL. The coefficient of variation was about 12% for the measurement of Hg-P. For the measurement of RGHg, the coefficient of variation was around 27%. For mist chambers, Stratton et al. (37) have the side-by-side deployments yielded a variability of about 20%.

## Results and Discussion

**Total Gaseous Hg and Hg-P.** Total gaseous Hg and RGHg were simultaneously sampled on 9 of the 16 events. Concentrations of TGHg varied between 1.03 and 2.50 ng/m<sup>3</sup> with a mean value of  $1.83 \pm 0.43$  ng/m<sup>3</sup>. The mean value falls in the range of the proposed background value of TGHg for this latitude (1.5–2.0 ng/m<sup>3</sup>, refs 15 and 44). Also, this value is close to the mean value of a larger TGHg database collected at the same site ( $1.89 \pm 0.94$  ng/m<sup>3</sup>, Table 1). Higher TGHg concentrations (> 2 ng/m<sup>3</sup>) were detected in October of 1999 while lower values (< 2 ng/m<sup>3</sup>) were found in the summer months (June–August). Similar seasonal trends have been observed in central and northern Europe, upstate New York, and St. Lawrence River valley by other groups (33, 45, 46). Possible explanations for this trend include lower mixing heights in winter, higher fuel demand for heating and thus higher Hg emission in winter, or higher Hg<sup>0</sup> oxidation rate in summer.

TABLE 1. Estimate of Dry Deposition Fluxes of Various Atmospheric Hg at Chesapeake Biological Laboratory

species	conc (ng/m <sup>3</sup> ) <sup>a</sup>	V <sub>d</sub> (cm/s) <sup>c</sup>	flux (ng m <sup>-2</sup> h <sup>-1</sup> )	refs
Hg <sup>0</sup>	$1.89 \pm 0.94$	0.00–0.09	0.00–6.12	14, 36, 53
RGHg <sup>b</sup>	$0.04 \pm 0.05$	0.13–4.83	0.19–6.96	14, 30, 32, 33, 36, 54, 55
Hg-P <sup>b</sup>	$0.02 \pm 0.05$	0.02–0.20	0.01–0.14	32, 33, 36, 54

<sup>a</sup> These values are the mean and standard deviation of samples collected between 1997 and 1999. <sup>b</sup> RGHg and Hg-p were samples using the filter pack method. <sup>c</sup> V<sub>d</sub> means dry deposition velocity.

The concurrently sampled RGHg made up 0.2–29.5% of the TGHg. On 6 of the 9 sampling events, RGHg made up less than 5% of the TGHg. High RGHg/TGHg ratios (0.06–0.30) were only observed on 8/4/98 and 8/5/98, but no elevated TGHg was observed at the same time. Particulate Hg was sampled whenever the filter pack was deployed, and it ranged from less than the detection limit (9 pg/m<sup>3</sup>) to 147 pg/m<sup>3</sup> on the 9 sampling events when TGHg was also sampled. Samples collected on 8/4/98 and 8/5/98 showed higher Hg-P/TGHg ratios (0.01–0.08) compared to the other samples (<0.005). These results may suggest that our air sampling were influenced by local sources of Hg-P and RGHg on 8/4/98 and 8/5/98.

**Comparison between Filter Pack and Mist Chamber.** A total of 14 field RGHg sampling comparisons between filter pack and mist chamber methods were conducted in July and August of 1998 and in August and October of 1999 (Figure 2). Each mist chamber bar in Figure 2 represents the mean of 3 (e.g., 8/4/98) to 13 (e.g., 8/26/99) consecutive samples. The error bars therefore indicate temporal variability, not analytical error. The data showed reasonable agreement between these two methods given the fact that (i) concentrations are generally low (<100 pg/m<sup>3</sup>) and (ii) the differences in sample collection time, 2 h for mist chamber and 6–24 h for filters. Both sampling methods demonstrated a wide variation of RGHg concentration in the ambient air, and concentrations generally varied in a similar fashion. The mist chamber had the highest RGHg concentration on 8/5/98 and the lowest value on 10/28/99 (below the detection limit). The discrepancy between these two methods was more significant when the RGHg was high, especially on 7/30/98 and 8/5/98 where the mist chamber values were higher, but also highly variable (Figure 2). Linear regression of these data generated an equation with a slope of 1.34 (*p* = 0.0008), an intercept of –3.80 (*p* = 0.925), and a *R*<sup>2</sup> of 0.62 (Figure 3). While the hypothesis was that both methods would collect the same amount of RGHg (slope = 1 and intercept = 0), the regression result indicated that the mist chamber collected 34% more RGHg on average than the filter pack. One possible explanation for the difference is that the cation-exchange membrane may not capture RGHg efficiently under high RGHg concentration. However, the analysis of the second (backup) membrane did not show any measurable RGHg signal, suggesting that there was no breakthrough. An alternative explanation for this discrepancy is the in situ oxidation of Hg<sup>0</sup> inside the mist chamber during sampling. Although they found no significant reaction in the presence of ozone, Stratton et al. (37) suggest a potential for a positive bias in mist chamber measurements as suggested by our data.

An unusual depletion of TGHg in the Arctic surface air has been observed following polar sunrise in spring (47). The Hg temporal trend resembled the temporal fluctuating pattern of ozone that was sampled concurrently. If the chemical compounds, mainly reactive halogen species, which are responsible for the ozone depletion, are also responsible

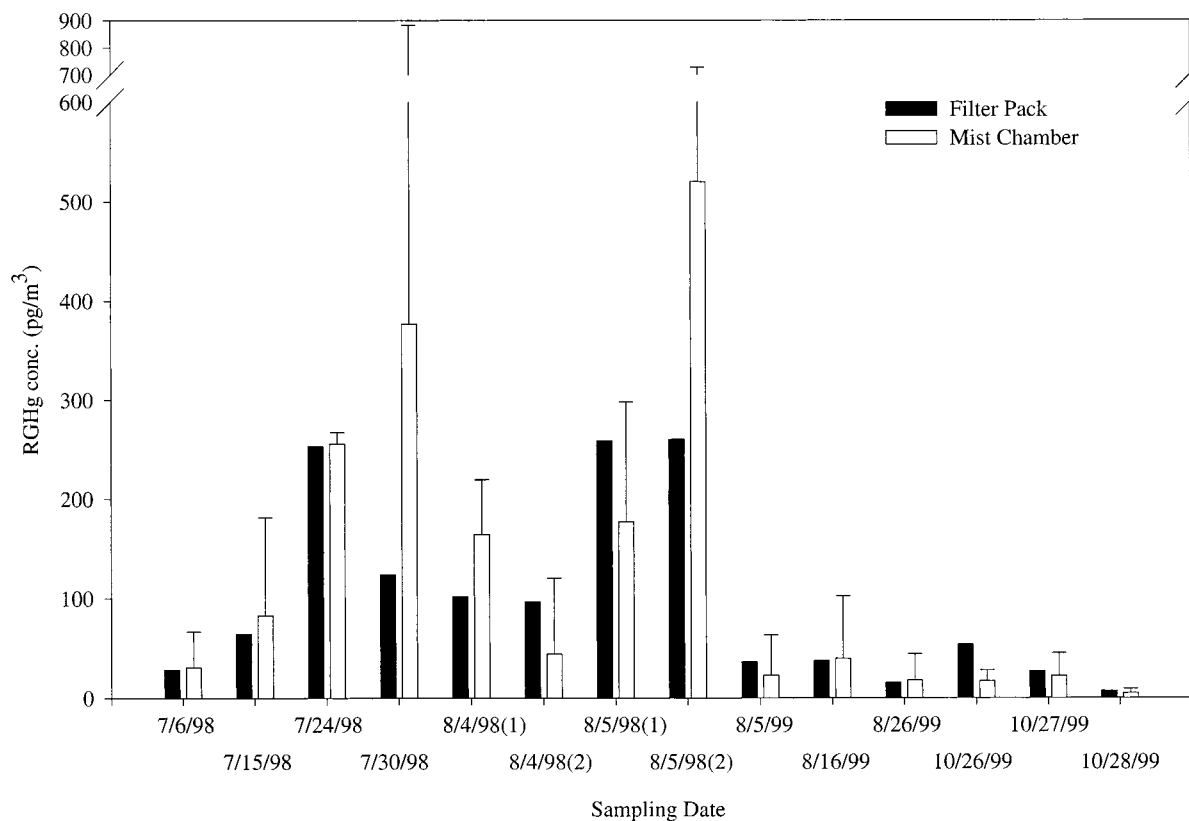


FIGURE 2. Comparison between filter pack and mist chamber collected RGHg.

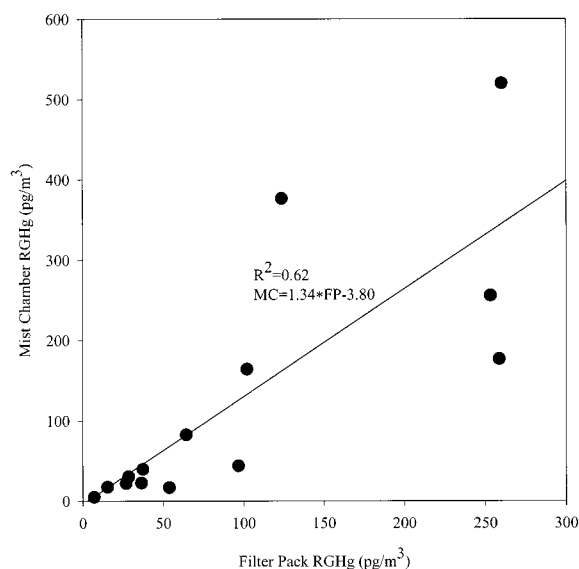


FIGURE 3. Linear regression between mist chamber and filter pack collected RGHg.

for the TGHg depletion, then similar types of reactions could also occur inside the mist chambers at CBL. Reaction mechanisms have been proposed for the production of reactive halogen species (e.g., BrCl, Br atom, and Cl atom) in the marine boundary layer (48–51) and high concentration of molecular chlorine, the precursor of Cl atom, has been detected in coastal air (52). These species could be strong  $Hg^0$  oxidants in the marine boundary layer. Under typical environmental conditions, these reactive halogen species might be enriched in the coastal air and scavenged by the scrubbing solution to react with  $Hg^0$  or other reduced forms of Hg inside the mist chamber. These reactions would therefore occur even if the mist chamber was shielded from

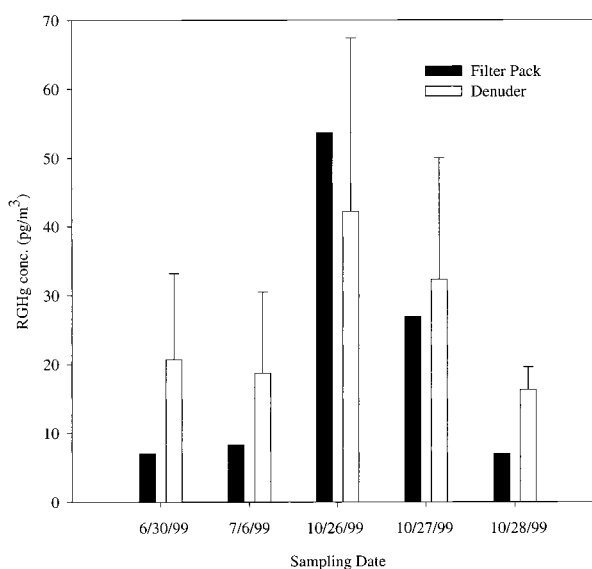


FIGURE 4. Comparison between filter pack and denuder collected RGHg.

light. The extent of these reactions at CBL would be a function of wind direction, and under most conditions, air masses passing over CBL are terrestrial rather than oceanic.

**Comparison between Filter Pack and Denuder.** Five RGHg sampling comparisons between the filter pack and the denuder methods were performed in 1999 (Figure 4). The average denuder value represents the mean of 3–12 consecutive samples. Again, the error bar reflects temporal rather than analytical variability. Both methods gave the same concentration range and temporal trend of RGHg, with the highest value collected on 10/26/99 (Figure 4). The denuder values were higher than filter pack on 4 of the 5 comparisons. Other groups sampling at Mace Head, Ireland

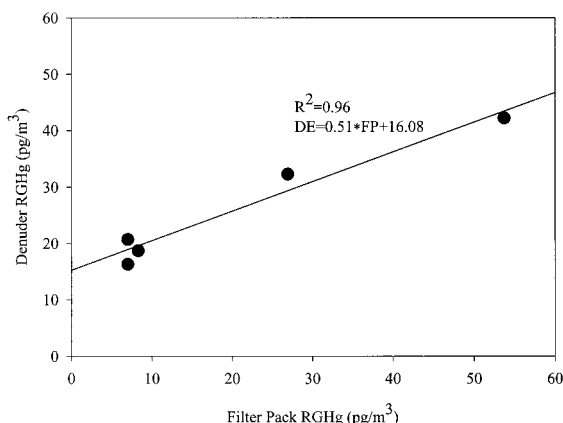


FIGURE 5. Linear regression between filter pack and denuder collected RGHg.

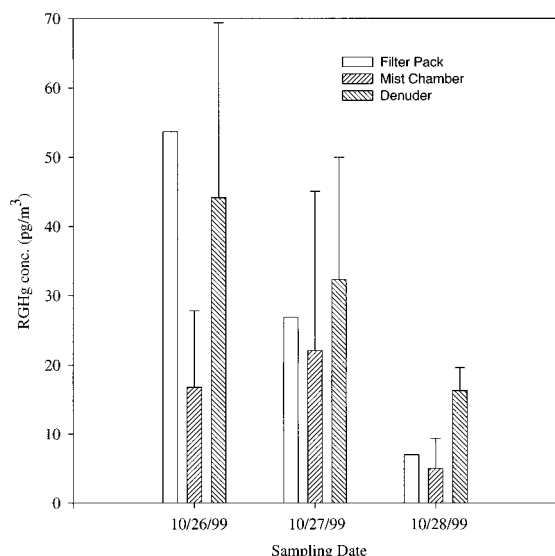


FIGURE 6. Comparison of RGHg collected by all three methods.

(17), also have found higher denuder values in comparison with the filter pack. Linear regression of our data gave a slope of 0.53 ( $p = 0.004$ ) and an intercept of 16  $\text{pg}/\text{m}^3$  ( $p = 0.003$ ) with a  $R^2$  of 0.96 (Figure 5). The regression result suggests that denuders are reporting higher values of RGHg relative to the filter packs at low RGHg. This probably indicates an inherent blank problem or the potential for adsorption or oxidation of  $\text{Hg}^0$  at the KCl surface as a result of heterogeneous reactions forming reactive halides, as has been suggested for sea salt particles (48–51).

A field blank for the denuder method was obtained by connecting a denuder to the sampling train for 2 h on the CBL research pier with the pump off. Analysis of this field blank showed no measurable Hg signal. The combination of zero field blank and higher denuder RGHg as compared to the filter pack suggests that, if it is occurring, the adsorption or oxidation of  $\text{Hg}^0$  at the KCl surface only occurs during sampling.

**Comparison among All Methods.** A three-way comparison of samplers deployed side by side was performed on 10/26/99, 10/27/99, and 10/28/99 (Figure 6). All three methods showed the same concentration range of RGHg. However, while the filter pack and denuder methods showed decreasing RGHg trend from 10/26 to 10/28, the mist chamber-collected RGHg peaked on 10/27/99 (Figure 6). Mist chamber concentrations were always the lowest during this sampling period. To some degree, these results contrast the two-way comparisons where both mist chamber and denuder

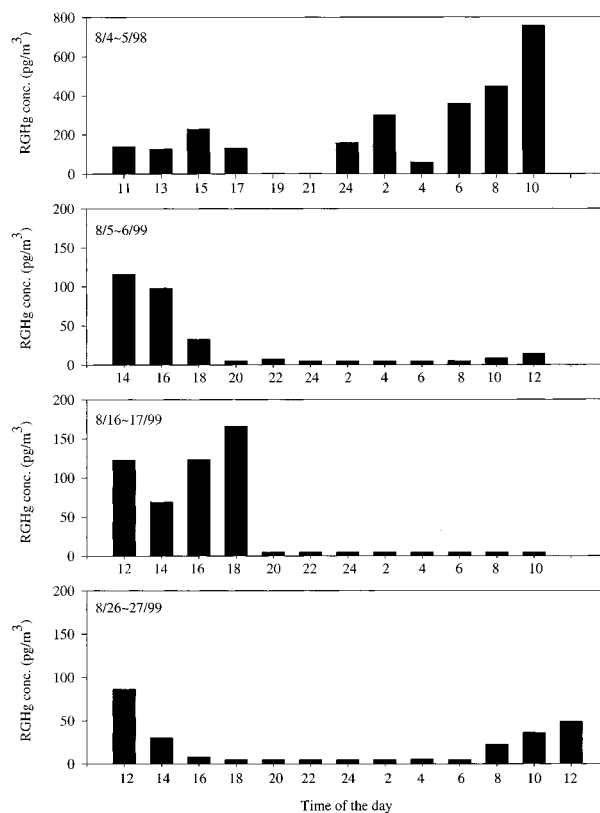


FIGURE 7. Diurnal trend of RGHg sampled by mist chamber.

concentrations were greater overall than the filter pack concentrations. Considering the uncertainties associated with making these measurements and the differences in sampling times, the data still reflect acceptable agreement among the three methods given the observed variability in concentration with time (see below).

**Diurnal Distribution of RGHg.** Seven 24-h RGHg sampling sessions were conducted using either the mist chamber (Figure 7) or denuder (Figure 8). Lindberg and Stratton (36) have demonstrated a diurnal cycle of RGHg with peak concentrations at midday and lower concentrations at night. Our data showed that the nighttime RGHg concentrations were generally lower than the detection limit (Figures 7 and 8). A clear diurnal RGHg pattern was observed only on one (8/26–27/99, Figure 7) of our seven 24-h sampling sessions, with RGHg elevated at midday, undetectable at night, and increasing again after sunrise. The lack of a clear diurnal pattern suggests that factors other than atmospheric chemistry are also influencing the production and removal of RGHg at CBL, such as meteorological conditions (e.g., wind speed and direction), and the resultant differences in concentration related to different air mass sources.

**Implications.** Published data of RGHg in ambient air are scarce in part due to the lack of reliable sampling techniques in the past. Nevertheless, the situation has improved with the development of the three methods in recent years. There are few published RGHg data (17, 36, 41), and as they are collected by different methods, it is difficult to make direct comparison with these data. Here we have demonstrated that these methods are able to quantify atmospheric RGHg at a picograms per cubic meter level and to track temporal RGHg trends with good agreement. The higher flow rate enables the mist chamber and denuder to collect RGHg over shorter time intervals, which allows better time resolution of the temporal distribution of RGHg. This sampling method development is important as our estimate of the dry depositional flux of Hg showed that RGHg could make up a

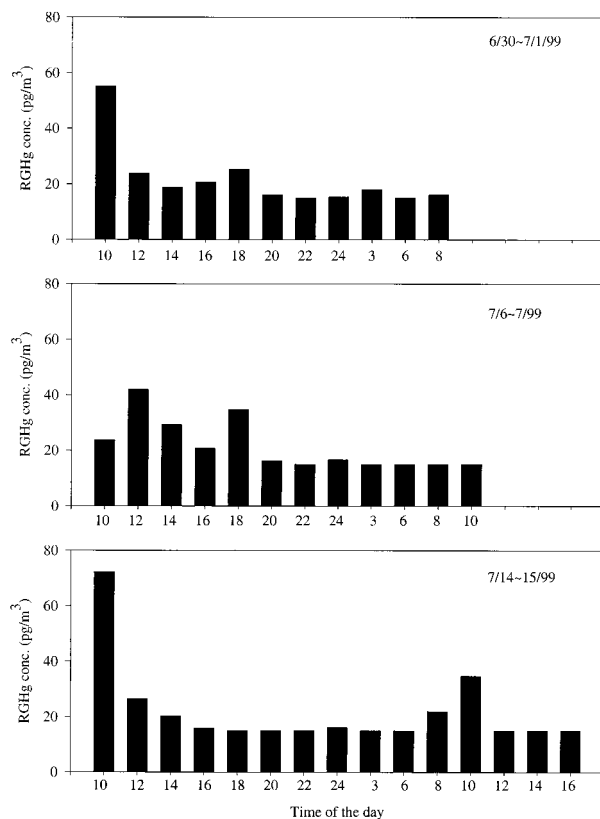


FIGURE 8. Diurnal trend of RGHg sampled by denuder.

significant portion of the total dry deposition (Table 1) even though RGHg is only a few percent of TGHg in the atmosphere. It is apparent that dry deposition of RGHg should be considered in studies of air–water or air–land exchange of Hg as it could be a significant factor influencing the biogeochemical cycling of Hg. On the other hand, although all the methods reported similar temporal trend of RGHg in this study, the reported values were not in complete agreement with each other, as indicated by the slopes of the regression equations. This study also did not demonstrate that all the ambient RGHg was collected by these sampling methods. We can only say that part of the ambient RGHg is very water-soluble and can be captured by the ion-exchange membrane and by KCl. More intercomparison studies conducted under different environmental conditions would definitely be helpful in exploring the likely biases between methods and thus the limits of their use.

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